

# FUNCTIONALIZATION OF SUPPORTED Au<sub>11</sub> NANOCCLUSERS THROUGH LIGAND EXCHANGE AND COMPARISON TO LIQUID PHASE REACTIONS

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## INTRODUCTION

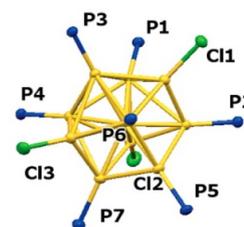
The properties of ligand protected Au nanoclusters are known to depend on both the size and composition of their metal core<sup>[1]</sup>, as well as on the nature of the surrounding ligands. This allows to synthesize clusters with various polarities or solubilities, and also different activity in catalytic reactions<sup>[2]</sup>. Therefore, tuning of cluster catalysts can be achieved by modifying their ligand shell in so called ligand exchange reactions<sup>[3]</sup>.

Although these reactions have been studied widely in the last years, their application has so far been limited to free clusters in solution. For heterogeneous catalytic applications of Au nanoclusters, they are usually immobilized on powder materials, as these catalysts exhibit significantly higher stability and enhanced activity<sup>[4]</sup>. However, the possibility of introducing new ligands onto supported clusters and therefore, modifying their properties, has not been evaluated so far.

## EXPERIMENTAL

In order to investigate the ligand exchange behavior of already immobilized Au nanoclusters for the first time, ligand exchange of Au<sub>11</sub>(PPh<sub>3</sub>)<sub>7</sub>Cl<sub>3</sub> (Figure 1) with monodentate thiol ligands was chosen as a model reaction. This specific reaction is well studied in liquid phase and known to lead to either partially or fully ligand exchanged Au<sub>25</sub> clusters (depending on the thiol used)<sup>[5,6]</sup>. Moreover, it allows easier investigation of the reaction outcome due to different elements (P and Cl vs. S) coordinating to the Au core prior to and after ligand exchange.

For our experiments, Au<sub>11</sub>(PPh<sub>3</sub>)<sub>7</sub>Cl<sub>3</sub> was synthesized with modifications to previous procedures<sup>[6]</sup>. The clusters were subsequently deposited on surfaces (Al<sub>2</sub>O<sub>3</sub> and ZnSe) as dropcast films or impregnated on oxide powders (SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>). These samples of immobilized clusters were then exposed to solutions of the exchange ligand. Both *in-* and *ex-situ* characterization was performed, using several spectroscopic techniques (UV-Vis, IR, PM-IRRAS, NMR, XPS, MS). For the powder samples, element specific analysis was done with ICP-OES, allowing determination of the degree of exchange.



**Figure 1:**  
Au<sub>11</sub>(PPh<sub>3</sub>)<sub>7</sub>Cl<sub>3</sub><sup>[6]</sup>

## RESULTS AND DISCUSSION

The supported Au<sub>11</sub>(PPh<sub>3</sub>)<sub>7</sub>Cl<sub>3</sub> showed very different behavior in the ligand exchange reactions compared to free clusters. For the cluster dropcast films on planar surfaces, which were monitored with PM-IRRAS (Figure 2) and ATR-IR, incomplete exchange was noticed. This was indicated by additional bands appearing in the spectra with reaction progress, which could be assigned to characteristic vibrations of the incoming thiol ligand. The MALDI-MS spectra recorded of the products demonstrated that the number of Au atoms in the core remained constant throughout the reaction. This is a

significant difference to ligand exchange in solution, where a growth to Au<sub>25</sub> was evidenced.

For Au<sub>11</sub>(PPh<sub>3</sub>)<sub>7</sub>Cl<sub>3</sub> supported on oxide powders, a clear change in sample color and UV-Vis absorption features indicated structural changes upon ligand exchange. As suggested by HAADF-STEM, the core size was again maintained, and ICP-OES measurements indicated incomplete exchange. These results are in good agreement with those of the dropcast films and further affirm the substantial differences between free clusters in solution and immobilized clusters on support materials. It is assumed that the interaction between the Au nanoclusters and the substrate has distinct influence on their ligand exchange activity, resulting in different products.

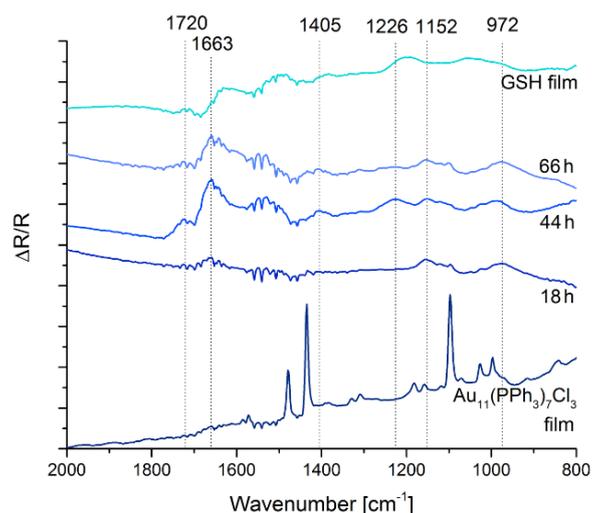
## CONCLUSION

Au nanoclusters supported on powders with high surface area are interesting candidates for catalytic activity studies. In this work, the possibility of post-functionalization of already immobilized clusters by ligand exchange was confirmed. As this allows to selectively modify the properties of nanocluster catalysts, it is likely to find broad application. In addition, it could be shown that the product of the ligand exchange with free clusters in solution versus supported clusters is significantly different.

Further studies of ligand exchanges with immobilized clusters will be performed to gain more insight into the bonding motive between cluster and substrate and the role of the ligands within that. In addition, chiral exchange ligands will be used in a next step, leading to chiral cluster catalysts.

## REFERENCES

- [1] Takano, S.; Tsukuda, T.: 'Controlled Synthesis: Size Control'. In: Protected Metal Clusters: From Fundamentals to Applications, Frontiers of Nanoscience vol. 9, 9-38, Elsevier, 2015.
- [2] Wan, X.-K.; Wang, J.-Q.; Nan, Z.-A.; Wang, Q.-M.: 'Ligand effects in catalysis by atomically precise gold nanoclusters'. Sci. Adv., 3 (10), e1701823, 2017.
- [3] Niihori, Y.; Hossain, S.; Kumar, B.; Nair, L. V.; Kurashige, W.; Negishi, Y.: 'Perspective: Exchange Reactions in Thiolate-Protected Metal Clusters'. APL Mater., 5, 053201, 2017.
- [4] Zhang, B.; Kaziz, S.; Li, H.; Hevia, M. G.; Wodka, D.; Mazet, C.; Bürgi, T.; Barrabés, N.: 'Modulation of Active Sites in Supported Au<sub>38</sub>(SC<sub>2</sub>H<sub>4</sub>Ph)<sub>24</sub> Cluster Catalyst: Effect of Atmosphere and Support Material'. J. Phys. Chem. C, 119 (20), 11193-11199, 2015.
- [5] Shichibu, Y.; Negishi, Y.; Watanabe, T.; Chaki, N. K.; Kawaguchi, H.; Tsukuda, T.: 'Biicosahedral Gold Clusters [Au<sub>25</sub>(PPh<sub>3</sub>)<sub>10</sub>(SC<sub>n</sub>H<sub>2n+1</sub>)<sub>5</sub>Cl<sub>2</sub>]<sup>2+</sup> (n= 2-18): A Stepping Stone to Cluster-Assembled Materials'. J. Phys. Chem. C, 111 (22), 7845-7847, 2007.
- [6] McKenzie, L. C.; Zaikova, T. O.; Hutchison, J. E.: 'Structurally Similar Triphenylphosphine-Stabilized Undecagolds, Au<sub>11</sub>(PPh<sub>3</sub>)<sub>7</sub>Cl<sub>3</sub> and [Au<sub>11</sub>(PPh<sub>3</sub>)<sub>8</sub>Cl<sub>2</sub>]Cl, Exhibit Distinct Ligand Exchange Pathways with Glutathione'. J. Am. Chem. Soc., 136 (38), 13426-13435, 2014.



**Figure 2:** PM-IRRAS spectra recorded over the duration of the ligand exchange reaction.